THE ORIGIN OF NI-BEARING SULFIDES IN CI CARBONACEOUS CHONDRITES,
D.S. Lauretta[1,2], K. Lodders[1,2], B. Fegley, Jr.[1,2], and D. T. Kremser[2]. [1]Planetary Chemistry Laboratory and [2]Dept. of Earth & Planetary Sciences Washington University, St. Louis, MO 63130-4899 USA.

Introduction. Experimental studies of sulfide formation in H_2-H_2S gas show that sulfurization of an FeNi alloy does not change the bulk Fe/Ni ratio of the metal. Instead, the Fe/Ni ratio of the resulting sulfides is equal to that of the metal. This is in contrast to thermodynamic equilibrium calculations which predict that sulfide formation in the solar nebula produced Ni-free troilite (FeS) and enriched the remaining metal in Ni [1-3]. Our data show that the Ni content of the sulfide layer increases with distance from the metal. The outer edge of the sulfide layer is enriched in Ni and is composed of both the monosulfide solid solution (mss) and pentlandite. These results suggest that mss and pentlandite formed concurrently in the solar nebula. The experimental sulfides are compositionally and morphologically similar to sulfides in the Alais CI chondrite [4], suggesting that these meteoritic sulfides are solar nebula condensates.

Experimental Procedure. Sulfurization experiments were done by heating slabs of the Canyon Diablo iron meteorite ($Fe_{93.4}Ni_{6.3}Co_{0.3}$) at 285, 340, or 370 °C under a controlled atmosphere containing 50 ppm H_2S in ultra high purity H_2. In the solar nebula $Fe_{94.1}Ni_{5.6}Co_{0.3}$ metal reacts with H_2-rich gas containing 33 ppm H_2S [5,6]. Condensation calculations predict that troilite forms at 437°C and 50% of S is condensed at 401°C [7]. The samples were analyzed by optical microscopy, X-ray diffraction, and electron microprobe. A broad electron beam was used on the metal and sulfide to determine their bulk Fe/Ni ratio and a focused beam was used to determine the variation of the Fe/Ni ratio within the metal and sulfide.

Results. Figure 1 shows the average bulk Fe/Ni atomic ratios and 2σ uncertainties for unreacted metal, partially reacted metal, and product sulfide layers. The Fe/Ni ratios of reacted metal and sulfide are the same at all temperatures studied. This is not predicted by thermodynamic equilibrium but is a result of the kinetic pathway for alloy sulfurization. The relationship between thermodynamics and kinetics is best illustrated by the diffusion path concept [8]. A diffusion path traces the composition of the metal-sulfide assemblage on the Fe-Ni-S ternary phase diagram, thus indicating the sequence and composition of phases. We determined the diffusion path for an experimental sample by measuring the compositional variation with an electron microprobe traverse starting at the unreacted metal core and ending at the outer edge of the sulfide layer. The compositional variation is plotted on the phase diagram shown in Figure 2. The probe data indicate four different compositional regions in the metal-sulfide assemblage. The boundaries between these regions are labeled a-e in Figure 2. At point a the Ni content is that of unreacted Canyon Diablo. Between a and b, the Ni content of the metal increases to ~30 wt% Ni over a distance of ~50 nm. We could not measure the enrichment of Ni over such a small distance. However, both the relative cation diffusion rates and the sulfide composition at the metal interface suggest the existence of a region of Ni-enriched metal. The dashed line connecting b and c indicates thermodynamic equilibrium between metal and sulfide at the interface and does not represent spatial extent. Mss containing ~0.6 wt% Ni (point c) is in equilibrium with FeNi metal containing ~30 wt% Ni (point b). The curve connecting c and d in Figure 2 follows the S-poor boundary of the mss stability field and indicates that the Ni content of the sulfide layer increases away from the metal. Beyond d, the curve enters the mss-pentlandite coexistence field. This corresponds to the outer edge of the sulfide layer which is composed of both mss containing 1-3 wt% Ni and pentlandite containing ~ 30 wt% Ni. The morphological relationship between pentlandite and mss is shown in Figure 3. Pentlandite appears as small inclusions within larger mss crystals.

Reaction Mechanisms. Our results suggest the following mechanisms for sulfide formation in the solar nebula. The composition of the sulfide depends on thermodynamic equilibrium at the metal-sulfide and sulfide-gas interface and on the cation diffusion rates in metal and sulfide. Thermodynamic calculations show that the sulfide in equilibrium with a solar composition Fe-Ni alloy is FeS. Initially, Ni-free troilite forms. Troilite formation selectively removes Fe and increases the amount of Ni in the metal at the metal-sulfide interface. In order for troilite formation to continue Fe atoms must diffuse through the Ni-enriched metal and the overlying FeS layer to reach the outer edge of the sulfide and react with the gas

[9]. However, the rate of Fe diffusion in the metal is ~12 orders of magnitude slower than in the sulfide [9,10]. If troilite were the only sulfide to form then the reaction rate would be limited by the rate of Fe diffusion in the Ni-enriched metal. However, the sulfide in equilibrium with the Ni-enriched metal is not Ni-free troilite but Ni-bearing mss. Thus, slow cation diffusion in the metal prevents the continuous supply of Fe atoms and halts the formation of troilite. Instead, sulfides form that contain Fe and Ni in the same proportion as the initial metal. In order to form mss both Fe and Ni cations must diffuse through the sulfide layer to the sulfide-gas interface. Ni diffuses almost twice as fast as Fe leading to an enrichment in Ni at the outer edge of the sulfide [11,12]. Eventually, the Ni concentration at the outer edge of the sulfide layer is high enough for pentlandite to be stable.

Implications. In our experimental sulfides, pentlandite containing ~30 wt% Ni appears as small grains within larger pyrrhotite crystals containing 1-3 wt% Ni (Figure 3). Kerridge and coworkers [5] report sulfide grains of this composition and morphology in the matrix of the CI-chondrite Alais (see Figures 2 and 5 in [5]). They concluded that these sulfides were not nebular products because troilite was predicted to be the main nebular sulfide. Here we suggest that these sulfides may indeed be pristine nebular condensates.

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Figure 1

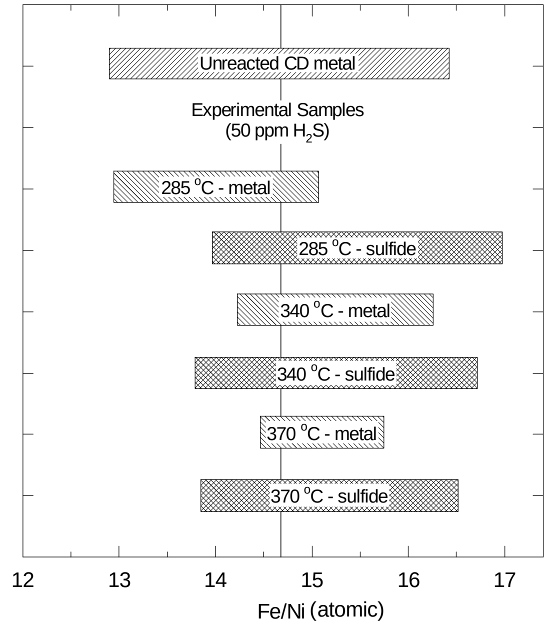

Figure 2

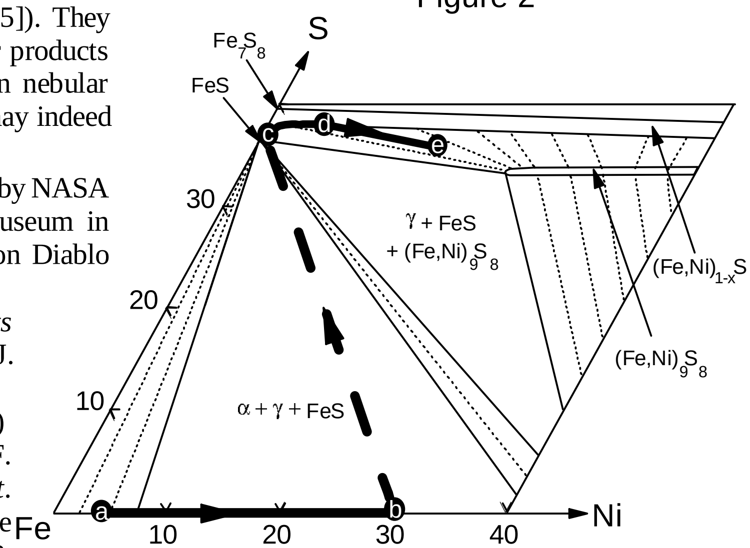

Figure 3